STUDIES ON FLUIDIZED BED TECHNOLOGY FOR TREATMENT OF GASEOUS POLLUTANTS:SULPHUR DIOXIDE

A Thesis Submitted to the

National Institute of Technology, Rourkela

In Partial Fulfillment for the Requirements

Of

BACHELOR OF TECHNOLOGY DEGREE

In

CHEMICAL ENGINEERING

By

UDITA RINGANIA

Roll no. 111CH0085

Under the guidance of

Dr. (Mrs.) Abanti Sahoo

Department of Chemical Engineering

National Institute of Technology

Rourkela-769008

CERTIFICATE

This is to certify that B.Tech. (Research) thesis entitled, "**STUDIES ON FLUIDIZED BED TECHNOLOGY FOR TREATMENT OF GASEOUS POLLUTANTS:SULPHUR DIOXIDE "** submitted by **Miss. Udita Ringania** in partial fulfillments for the requirements of the award of Bachelor of Technology degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance. She has fulfilled all the prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere.

Supervisor
Dr. (Mrs.) Abanti Sahoo
Department of Chemical Engineering,
National Institute of Technology,
Rourkela - 769008,
Orissa

ACKNOWLEDGEMENT

I feel immense pleasure and privilege to express my deep sense of gratitude and feel indebted towards all those people who have helped, inspired and encouraged me during the preparation of this report.

I am grateful to my supervisor, **Prof. Abanti Sahoo**, for her kind support, guidance and encouragement throughout the project work and also for introducing me to this topic.

I am also very thankful to all the staff and faculty members of Chemical Engineering Department, National Institute of Technology, Rourkela for their consistent encouragement and help throughout the project.

I would also like to extend my sincere thanks to my seniors especially Mr. Harjeet Nath or his unconditional support and assistance in the project.

Last but not the least; I would like to thank whole heartedly my parents and family members whose love and unconditional support, both on academic and personal front, enabled me to see the light of this day.

Thanking You

Udita Ringania

Rollno.111CH0085

CONTENTS

List of Tables

List of Figures

ABSTRACT

In a Fluidized Bed Reactor, which can be operated till a maximum of 500ºC, abatement of sulphur dioxide needs to be done. The bed material chosen is manganese ore. The main fluidizing gas is compressed air and the sulphur dioxide is fed as the secondary fluidizing fluid. The oxides of sulpure are prepared in the laboratory itself. Along with sulphur dioxide, oxides of nitrogen is also fed as the secondary gas for some of the experiments to check its effect on the abatement of oxides of nitrogen. Other than that temperature is also varied to see its effect. The residence time is another factor on which quality of fluidization depends hence it is also varied to check its effect on the abatement of sulphur dioxide. Finally the characterization of the bed material before and after fluidization is done and compared to confirm the reduction in the quantity of sulphur dioxide from what is initially fed to the Fluidized Bed Reactor.

Chapter 1

Introduction

1.1 Abatement of Oxides of Sulphur (SO_x)

The recent boom in the industrialization has had many advantages for the human civilization but it does not come without its adversities. The continuous increase in the use of fuels and oils in the industries has massively contributed to air pollution by releasing a series of toxic to the atmosphere at a rate which has only increased in the past 50 years. The air today is more polluted then ever and there is hardly any fresh air to breath. The increased exposure to the toxics has called for more studies to be carried out to abate these toxics from the air. The oxides of sulphur are among these toxics and a detailed study for their abatement is required.

Sulphur is a very common impurity that is encountered in the natural fuels (coal) and oil derived feedstock. When these fuels undergo combustion, they release the sulphur as sulphur oxides (SO_x) with the flue gas. Oxides of sulphur includes sulphur dioxide, sulphur trioxide, sulphur monoxide etc. Sulphur dioxide is an invisible gas with a sharp pungent smell.

Once released in the atmosphere, these SO_x then undergoes further oxidation causing a lot of side effects. Its interaction with the water causes acid rain which is known to have reverse effects on vegetation and also contributes towards poisoning of water bodies which in turn adversely affects the water life. Apart from these it also affects the human health and life. Sulphur dioxide enters the body through the respiratory system and low concentrations causes eye irritation, nose and throat irritation, tightness in throat and cough. High concentration of sulphur dioxide can cause severe problems like corneal haze, breathing difficulties, airway inflation. Physic alteration and even heart failures have been reported due to high concentration of sulphur dioxide.

Sulphur can either be removed before treating the crude oil by various methods of desulphurisation, or it can be abated from the flue gas before releasing it in the atmosphere. The strict regulations imposed by the pollution board of India on the amount of sulphur

oxides to be released in the atmosphere has made it necessary for the industries to treat the flue gas before releasing it in the atmosphere.

Abatement by Fluidized Bed is one of the recent techniques used for the removal of the oxides of sulphur and this study focuses on the removal of the sulphur dioxide using a fluidized bed reactor.

1.2 Fluidized Bed Technology

Fluidization is a phenomenon by which the solid bed particles behave as a fluid when a liquid or a gas is passed through the solid bed. The solid particles acquire the properties of fluid only when the fluid is passed through it with a minimum velocity which is required to balance the pressure drop across the static bed. This minimum velocity is known as the minimum fluidization velocity. Fluidization technique has known many industrial applications and it is preferred because of several advantages.

1.2.1 Advantages of Fluidized Bed Technology

Few advantages of using a FBR are as follows:

- It provides a better solid-fluid contact as compared to packed bed and trickle bed reactors.
- Due to better solid-fluid contact, higher rates of heat and mass transfer are observed.
- Due to the fluid like behavior of the solid bed the circulation between two adjacent reactors is easier. For example, in the case of catalytic cracking and regeneration combination the bed material is easily transferred from one reactor to the other.
- The reactor does not contain any moving mechanical part, hence the maintenance cost is reduced.
- Due to its vertical design, it occupies very low space in any industry.

- It can be used for continuous process and provides large throughputs.
- The fluidized bed is suitable for accomplishing heat-sensitive ,exothermic or endothermic reactions.
- Fluidised bed reactors are easy to handle even for large scale operations.
- Excellent heat transfer within fluidized bed makes it possible to be used as low surface area heat exchangers inside the bed.
- Multistage operations are possible, and hence the solids residence time as well as the fluid resistance time can be adjusted to desired levels.

1.2.2 Applications

Fluidized Bed Reactor has extensive industrial applications as can be seen in the above mentioned advantages. It is used in nuclear power plants, petroleum, chemical, bio-chemical and metallurgy industry. Fluidized-Bed Catalytic Cracking (FCC) is the most important and widely used refinery process for converting low value, heavy oils into more valuable gasoline and lighter products. In Petroleum industry, it is extensively used for fluid bed catalytic cracking, in chemical operations like gasification and carbonization of coal, roasting of sulphur ores, reduction of iron oxides, blending of granular materials, granulation of fertilizer, combustion, incineration, to form plastics from rubber, in acetone recovery, formation of polyethylene, to form styrenes from hydrocarbons and pyrolysis and in physical operations i.e. drying of solids such as crushed minerals, sand, polymers, pharmaceuticals, fertilizers and crystalline products, coating of metals with plastic and particles in pharmaceutical and agricultural industries, for transportation, granulation of solids, heating, cooling and water & waste treatment etc. The commercial applications of fluidization are in fluid catalytic cracking(FCC), reforming, Fischer-Tropsch synthesis, cement clinker production, calcination of aluminum hydroxide, catalyst regeneration, granulation (growing

particles) and drying of yeast, oxidation reactions involving solid catalyzed gas phase reactions, fluid coking, bio-oxidation process for waste water treatment and transportation of solids like slurry pipeline for coal.

1.3 Objective of the work

The objectives of the work has been listed as follows:

- To study the basic bed behaviors of the fluidized bed reactor
- To analyse the bed material before and after the reactions.
- To study the degree of abatement of sulphur dioxide by the bed material using the fluidized bed reactor.

CHAPTER- 2

LITERATURE SURVEY

Sulphur dioxide being a poisonous gas its concentration released in the atmosphere must be under check. Factory workers are the people who possess the maximum risk of sulphur dioxide inhalation. During any 8-hour work-shift of a 40-hour workweek, the average concentration of sulphur dioxide in the workplace must not exceed 5 ppm [1]. Many research has been carried out to abate the oxide before releasing it to the atmosphere. However, no method has yet been developed that can remove sulphur dioxide efficiently from the flue gas. Hence, research is still going on to find a better method.

2.1 Different Methods Available for the Abatement of SO_x.

Different methods have been used by industries as well as researchers for the abatement of SO_x. Some of these methods have been discussed below.

2.1.1 Abatement Using Limestone as a Sorbent.

Calcium carbonate has been used for the wet desulphurization[2]. The main reaction governing this process is:

$$CaCO_3 + 2SO_2 + H_2O \rightarrow 2Ca(HSO_3)_2 + CO_2 \qquad \text{-----Eq. (1)}$$

The desulphurization effect of $CaCO_3$ sorbent derived from South African limestone conditioned with fly-ash has been observed to improve the abatement efficiency [3].

There are many factors that affect the reactivity of limestone with SO_2 such as physical properties including porosity, hardness or grindability. Chemical properties like the presence of manganese upto 5% aids the reactivity, whereas, the presence of dolomite adversely effects the reactivity [4]. The limestone after desulphurization can be disposed-off as a solid waste which is an advantage of using it.

2.1.2 Abatement Using Coal Fly-ash.

Removal of SO_2 from flue gas by the absorbent synthesized from coal fly ash and calcium oxide was studied under different reaction conditions to elucidate the effect of the coexistence of NO and O_2 in the flue gas [5].NO and O_2 aided in the production of sulphate (SO_4^{2-}) ion instead of sulfite (SO_4^{3-}) ion. Fly-ash was also observed to increase the efficiency of calcium carbonate for removal of sulphur dioxide using a fixed bed reactor [3].

2.1.3 Abatement Using Activated Carbon.

Activated carbon is used extensively as an adsorbent for the removal of sulphur dioxide from air. The surface area of an activated carbon ranges between 700- 1200 m^2/gm which is around 7000 times greater than any un-activated carbonaceous material. They can be easily regenerated as well. However, the only disadvantage is that about 1000 tones raw material generates only about 100 tones activated carbon.

Various studies using activated carbon as fluidized bed material [6] as well as in a tickle bed reactor [7] has been studied. The activated carbon in the tickle bed reactor was regenerated using distilled water. The use of activated carbon as a activated carbon fiber has also been done in which the ACF can be used to continuously remove sulphur dioxide from an inert atmosphere without having to regenerate the fiber[8]

2.1.4 Abatement Using Hollow Fiber Membrane Contactor.

Hollow fiber membrane contactors are used as a contacting medium for the adsorption of SO_x from flue gas. The simultaneous removal of SO_2 and CO_2 from coal-fired flue gas has been carried out in a polypropylene hollow fiber membrane contactor using aqueous monoethanolamine as the absorbent [9]. PVDF (polyvinylidenefluoride) hollow fiber membranes have also shown efficient SO2 Removal [10].

2.1.5 Abatement Using Microorganisms.

The abatement of the sulphur dioxide by using microorganisms has been effectively carried out . Thiobacillus ferrooxidans or Desulfovibrio desulfuricans bacterium [11] is a type of sulphate reducing microbial which reduces sulphur dioxide to H_2S.

2.1.6 Abatement Using Fluidized Bed Technology.

In this method a suitable bed material is taken which has the affinity for either reacting with the oxides of sulphur or can adsorb it on its surface. The flue gas containing the oxide is passed through the bed as the fluidizing media. Due to better solid-fluid contact provided by fluidized bed reactors, the efficiency of abatement is greater compared to other abatement techniques.

Gas–solid fluidized beds have been widely used in both the chemical reactions and the physical processes for their excellent gas–solid contacting and relatively uniform temperature/ concentration profiles within the beds. Gas–solid circulating fluidized beds find wide application in the chemical and process industries, such as fluidized catalytic cracking (FCC) ,combustion ,alumina calcining, and synthesis of fine chemicals like maleic anhydride. More recently, liquid–solid circulating fluidized beds are also finding applications in the process industries such as in the synthesis of aromatic and olefinic alkylates.

2.2 Manganese Ore as a Bed Material

Most of the works of NO_x and SO_2 removal focuses on process either for SO_2 removal or NO_x reduction only, very few for simultaneous reductions. Techniques have been developed for simultaneous $DeSO_x/DeNO_x$ and can be categorized into two groups' namely: wet and dry techniques. Solubility of NO is low in aqueous solution. So, chemical scrubbings, as wet method, can't be used. In simultaneous dry removal process absorption for removal of SO_x

and selective catalytic reduction for removal of NO_x is considered to be a promising process [11]. Natural Manganese Ore (NMO), which is composed of various metal oxides, mainly manganese oxide, has the potential to be used as a sorbent catalyst in the simultaneous removal of SO_x/NO_x and has good abrasion resistance. Also it is low cost and does not need any kind of pre-treatment for its operation (other than crushing).

2.3 Utilization of Manganese Ore

The uses of NMO are (i) In the extraction of Manganese metal. (ii) Removal of Arsenic from gunpowder using low cost ferriginious manganese ore[11] (iii) Used in Chemical looping combustion- Effect of steam gasification[12] (iv)to abate fluoride from water[13]. The NMO can also be utilized for reducing NO_x and SO_x simultaneously.

2.4 Composition of NMO

A typical manganese ore contains Mn, Si, Fe, Al, Ca, Mg, Zr, and etc. The typical composition of NMO is given in table 2(a) [11]. The composition of manganese ore in different countries is given in table 2(b) [14]. The typical properties of NMO are given in table 2(c).

Tables

Table 2(a). Typical Concentration of NMO

Component	Mn	SiO_2	Al_2O_3	Fe	CaO	MgO	Balance Oxygen of Fe and Mn
Wt %	51.83	3.13	2.51	3.86	0.11	0.25	38.31

Table 2(b). Characteristic of Manganese Ore from Different Countries

Exporting country	Weight percentage, %								P/Mn	Standard fraction, mm
	Mn	Fe	P	SiO_2	Al_2O_3	CaO	MgO	K_2O		
Ukraine	21-32	1.5-3.1	0.13-0.21	38.0-40.0	3.4-4.0	1.4-2.9	1.4-2.1	1.5-1.8	0.006	–
Ghana	30-40	1.2	0.06-0.1	10.7-18.7	2.4-2.6	4.1-4.5	3.0-3.2	0.7-1.2	0.002	6-80
Gabon	45-51	3.2-4.7	0.08-0.11	5.0-7.8	5.5-5.8	0.1-0.35	0.08-0.2	0.7-1.2	0.002	6-100
Australia	50-57	5-6	0.08-0.1	3.6-11.5	3.3-5.2	0.1-0.2	0.1-0.2	0.7-1.2	0.002	3-100
Republic of South Africa	38-51	5-16	0.02-0.04	3.0-6.5	0.3-0.9	4.0-11.0	0.3-0.6	0.02-0.1	0.0007	6-75
Brasilia	43-50	3.3-9.0	0.05-0.12	2.0-8.0	3.7-10.8	0.2-3.5	0.3-3.0	1.0-1.5	0.002	6-75
India	30-40	9.0-20	0.05-0.1	5.0-7.0	5.0-8.0	2.0-3.0	1.0-2.0	NA	0.002	6-100

Table 2(c). Physical Properties of NMO

Physical Property	Value
Density(gcm^{-3})	3.98
Surface Area(m^2g^{-1})	20
Pore Volume(cm^3g^{-1})	0.0392(5-3000Å)
Average Pore Diameter(Å)	134.36

Chapter 3

Experimental Setup and Procedure.

Preliminary experiments were carried out in a column having the same dimensions as that of the fluidized bed reactor where the actual reactions were done (Fig.3.0). The minimum fluidization velocity was calculated (Fig 3.1) and the same air flow rate was taken as the minimum fluidization velocity for the experiment in the fluidized bed reactor. A fluidized bed reactor made of stainless steel designed by Nath [11] was used and set up in the laboratory. Manganese Ore of definite size was selected as the bed material. SO2 was produced in the laboratory. After that two sets of experiments were carried out where the SO2 produced was allowed to mix with the fluidizing gas thereby fluidizing the bed material. In the first case Reaction time is increased in intervals of 10 minutes, whereas in the second case the temperature of the bed was varied from 300^0C to 450^0C. The bed materials was fluidized using a compressor.

3.1 Experimental Set-Up for Fluidized Bed Reactor

Fig 3.2(a-h) and Fig 3.3 shows the different components of the experimental set-up and the schematic diagram of the experimental setup respectively. The reactor and the pipes used to build up the FBR was made up of Stainless Steel 316 grade and was fabricated with the help of Mechmomine Kolkata. It has a capacity to withstand a pressures upto 5 atm (506625 Pa) . The length of the reactor column was20.5" (0.5207m) and the internal diameter was 4" (0.1016m) with 0.39" (0.009906 m) thickness. The reactor was bounded in both the sides with cones of 4" (0.1016m) height and 4" (0.1016m) internal diameter, the thickness being same as the reactor column. The removable bolt joint between the cones and the reactor column was provided with iron heat gaskets to prevent leakage. A ceramic heater is connected to the periphery of the FBR which was capable of heating the FBR to a maximum temperature of 500^0C (773.15 K) diameter and 0.2" (0.00508m) thickness. The bases of the cones were provided with wired meshes of size approximately 40 microns (40x10-6m). This

wired mesh acts as the gas distributor in order to fluidize the bed materials. The reactor was also provided with two gate valves and one globe valve. The globe valve was used to maintain the air flow rate from the air blower. The gate valves were used to either allow the gas to circulate or stop it at certain points.

3.2 Sulphur Dioxide Production.

A laboratory setup was established to produce sulphur dioxide which was used to study the abatement of $S0_2$ by the manganese ore in the fluidized bed reactor. Concentrated sulphuric acid when reacted with copper turnings, in the presence of heat, generated sulphur dioxide, which was collected in a bladder by the upward displacement of air.

3.2.1 Experimental Setup

A round bottom flask of capacity 500 ml was used and it was fitted with a rubber cork. A thistle funnel was fitted through the cork to supply the concentrated H_2SO_4 in the flask. A glass rod was also passed through the cork and was connected to a gas bladder. Sulphur dioxide was collected in this bladder which was later used for studying the abatement in the fluidized bed reactor. The round bottom flask was set in an electrical heater to supply the necessary heat required for the reaction.

3.2.2 Procedure

Copper turning weighing 6.35 grams was added in the round bottom flask. The flask was then sealed using the cork so that no SO_2 escapes to the surrounding. Then 10.6 ml of 98% concentrated H_2SO_4 was added through the thistle funnel to the round bottom flask. As the reaction is endothermic in nature, heat has to supplied to the system. The electrical heater was turned on to supply the heat at 100 watts. Fumes of sulphur dioxide were produced which was carried through the glass rod to the gas bladder by the upward displacement of air. If all the cupper turning reacts with the acid, approximately 2.24 lt. of sulphur dioxide will be produced. However, the reaction does not reach completion for some unforeseen reasons. The

amount of SO2 produced can be calculated by weighing the amount of copper turnings left in the flask and estimating the quantity reacted. The equation governing this reaction is as follows:

$$Cu + 2H_2SO_4 \leftrightarrow CuSO_4 + 2H_2O + SO_2 \quad \text{--- Eq. (2)}$$

3.3 Materials and Methods

10 kilograms of natural manganese (NMO) ore was purchased by the local supplier and was used as the bed material.

3.3.1 Material Preparation

After the purchase of the manganese ore, its density was calculated by using the water displacement method (Archimedes principal). The ore was put in a beaker filled with water upto its brim. The water displaced by the ore was collected and measured and its density was calculated. After three runs, the average density found to be 3.384 grams/cm^3as shown in Table No. 3(a). Since the density was found to be 3.384 gm/cm3, the bed material can be either Geldart B or Geldart D particle. However, Geldart D particles are not a suitable choice for fluidization as it is prone to sprouting and mixing. Therefore, for smooth fluidization the particles must be Geldart B particles with size ranging from 40×10^{-6} m to 500×10^{-6} m.

The ore then underwent size reduction which took in two phase: (a) Crushing and (b) Grinding. Crushing was carried out using a jaw crusher to reduce the size of the ore so that they become suitable to be further grinded. The reduced size ore was further grinded using a ball mill. About 28-30 equal size balls were used in the ball mill and runs of intervals 30-45 minutes was carried out. This reduced the ore to the desired size range.

The ore was next sieved using a sieve-shaker. Maximum amount of particles were found in the range of 200 µm to 500 µm. Hence these particles were used as the fluidized bed materials. The samples of the ore were then sent for various analysis.

3.3.2 Characterization of Bed Material

The NMO sample is analyzed for knowing about different components present in it. After experiments the bed materials are also analyzed to confirm the results. The various elements present before and after the experiments are compared, and from these comparisons we can say that the reaction has taken place, due to which the composition have changed.

Bed material, which acts as one of the reactants, is of great importance without which the FBR cannot be designed. NMO with an average particle size of 360 microns is used. The small particle size provides adequate fluidization for NMO bed and more surface area for adsorption of the oxides of nitrogen.

3.3.3 Methods

Preliminary experiments were carried out with a Perspex column of the same inner diameter as the fluidized bed reactor (Fig: 3.1(a-b)). The behavior of the bed material in this column was noted as it would be the same for the FBR (Fig: 3.2 (a-f) and Fig: 3.3). The minimum fluidization velocity was calculated in this column and the same was used for the reactor as well. A bed height of 5 cm with 500 grams of the bed material was used in both the reactors. Experimentally the minimum fluidization velocity was found to be 8.5×10^{-2} m/sec at a flow rate of 40 LPM.

The voidage of the static bed was found to be 6.19×10^{-1} as shown in Table No.3 (b). The theoretical minimum fluidization velocity was calculated using the Ergun's equation where spherity of the particle was assumed to be 1. At high Reynolds number, the minimum velocity was found to be 5.7×10^{-2} m/sec which was close to the experimental velocity.

A minimum flow rate of 40 LPM was maintained in the FBR by using a compressor. The first experiment was carried out with 500grams of the bed material and at a temperature of 200^0C (473 K). SO2 was fed to the reactor with air as the primary fluidization medium. A residence

time of 15 minutes was maintained. The bed was then allowed to cool and the sample of the bed material was collected to be sent for XRD analysis. Two more runs were carried out at the same reaction conditions with residence times of 30 and 45 minutes.

The second experiment was carried out at 300^0C with a residence time of 30 minutes. The sample was collected and sent for XRD and SEM analysis.

Tables

Table No. 3(a): Density Calculation of NMO.

RUN NO	**WEIGHT OF THE ORE (gm)**	**VOLUME DISPLACED (ml)**	**DENSITY ($gm.cm^{-3}$)**	**AVERAGE DENSITY ($gm.cm^{-3}$)**
1.	250.410	74	3.384	3.36
2.	300.02	88	3.41	
3.	275.56	82	3.36	

Table No. 3(b): Voidage Calculation of bed material

Mass Taken (m) (gm)	Circumference of FBR = 2 x 3.14 x r (cm)	Radius of FBR (r) (cm)	Height of fluidized bed (cm)	Area of Cross Section (A)=3.14 x r^2 (cm^2)	Density (gm/cm^3)	Voidage = 1-(m/A x h x D)
500	31.25	4.97	5	77.71	3.384	0.619

FIGURES

(a) Static Bed.

(b) Fluidized Bed.

Fig. 3.1(a-b): Pictures of Fluidized Bed with NMO as Bed Material.

(a) **Front View of the Reactor column.**

(b) Top View of the Reactor .

(c) Top View of the Cone.

(d) Front View of the Cone.

(e) PID Controller.

(f) Actual Experimental setup.

Fig. 3.2(a-f): Pictures of Different Parts of Experimental Work.

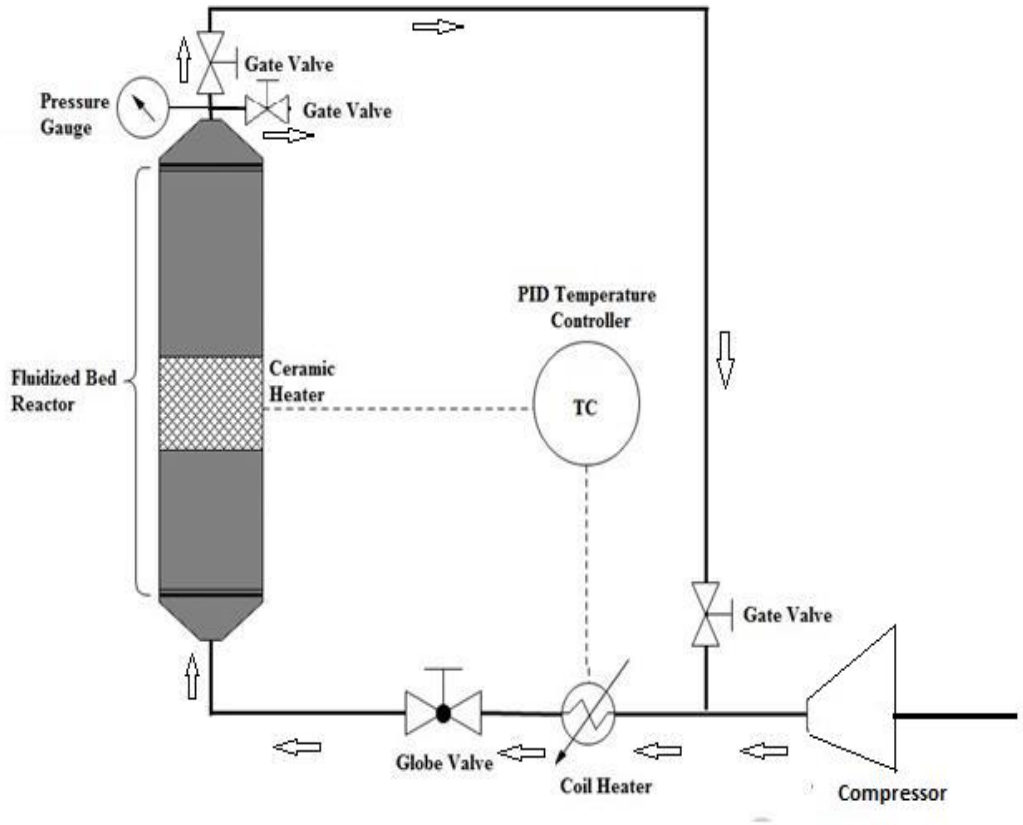


Fig. 3.3: Schematic diagram of the Experimental Setup

Fig. 3.4: Experimental setup for SO_2 production

Chapter-4

Results and Discussion

4.1 Analysis for Manganese Ore as bed material with or without flue gas treatment.

Preliminary study regarding the bed material and its characterization is very important to carry out the experiment. As literature indicates the oxides of sulphur will get adsorbed with the metal particles at high temperature, it is essential to know the characteristic of NMO at different temperatures for the present work. Depending on the results obtained from preliminary characterization of NMO, the further reactions in the fluidized bed are carried out accordingly.

4.1.1 Fluidization Parameter

Fluidization is one of the best methods of providing proper fluid-solid contact. Different aspects affect the quality of fluidization. Again many aspects are to be analyzed as prerequisites for proper fluidization. Minimum fluidization velocity is one of the aspects which is to be determined first. Preliminary experiments suggest that NMO particles of 320 microns size have good fluidization quality and is used as a bed material for the reaction. The theoretical value of the minimum fluidization velocity comes to be 5.7×10^{-2}m/s. From the experimental data for finding minimum fluidization velocity (Table No. 4(a)) a graph was plotted between ΔP (Kpa) and u (m/s) (Fig: 4.1) and the minimum fluidization velocity was found to be 8.5×10^{-2}m/s. It is almost same as the theoretical value.

4.1.2. Heating Process

Fig 4.2indicates the time taken by the FBR to reach the maximum temperature of 500^0C (773.15K). The reactor takes almost 42 minutes to attain a temperature of 200^0C (473.15K), 58 minutes to reach 250^0C (523.15K) and 93 minutes to reach 300^0C (573.15K).

4.1.3 XRD Analysis

The major components at room temperature are manganese (Mn), Manganese Oxide (MnO_2), silicon dioxide (SiO_2), Calcium Oxide (CaO), Iron (Fe), Aluminium Oxide (Al_2O_3), and Magnesium Oxide (MgO). The XRD pattern (Fig:4.2) of the elements are referred form

JCPDS file of X'PertHighScore software. Using peak broadening technique of X'Pert High Score software for XRD analysis, one can clearly differentiate the peaks. The Peaks of Mn are coming at around 28.68º, 37.33º and 56.65º. There are no traces of any Manganese nitrate from the XRD analysis.

The XRD analysis of the bed material run at 300^0C in the FBD reactor was done for the 2θ range of 20^0 to 60^0. The XRD analysis (Fig: 4.3) shows the presence of $MnSO_4$ which was not present before in the sample. $MnSO_4$ peaks where observed at the 2θ values of 23, 24 and 35. This presence of the $MnSO_4$ peaks confirms that sulphur dioxide is being abated from the gas phase.

The XRD analysis of the sample from other experiments run at 200^0C for different residence time show similar characteristics (Fig: 4.4 (a-c)). Also it was observed that more amount of sulphur dioxide was abated at 300^0C then compared to 200^0C. This is because at higher temperature the complex compounds of manganese break down to simple manganese oxides which then easily reacts with SO_2.

4.1.4 FESEM Analysis

For SEM analysis, known amount of the powdered sample is first dispersed in a volatile solvent like acetone and then few drops of mixture was dripped on a substrate surface. The sample is then dried ultrasonically and was then observed under Field Emission Scanning Microscope (FESEM). The FESEM sample of NMO sample before and after the reactions are observed as shown in Fig: 4.5 (a-b) It can be seen from the Fig: 4(a) that the particles are loosely packed with large amount of pores and are crystalline in nature.

The EDX analysis of the sample shown in Fig: 4.6 show the concentration of various components before and after the reactions. It can be seen that the concentration of sulphur increases after the reaction thus suggesting the successful abatement of sulphur dioxide from the gas.

Tables

Table No 4(a): Experimental Values for Calculation of Min Fluidization Velocity

Sl.No.	H1(mm)	H2(mm)	ΔH(mm)	ΔP (Kpa)	Flowrate (LPM)	Velocity (m/s)
1.	193.5	193.5	0	0	0	0
2.	190.6	196.4	5.8	0.75	10	0.021
3.	183.8	203.2	19.4	2.5	20	0.043
4.	179.5	207.5	28	3.63	30	0.064
5.	174.5	212.5	37.5	4.85	39	0.083
6.	175	212	37	4.79	40	0.085
7.	175	212	37	4.79	45	0.096
8.	175	212	37	4.79	50	0.11
9.	175	212	37	4.79	55	0.18

Figures

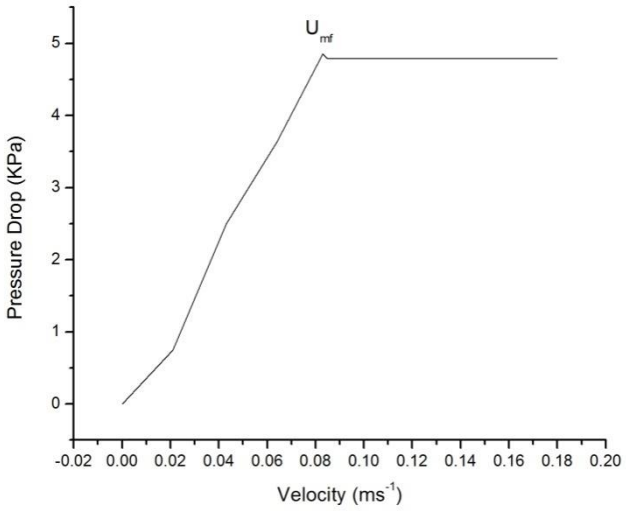


Fig.4.1: Minimum Fluidization Velocity

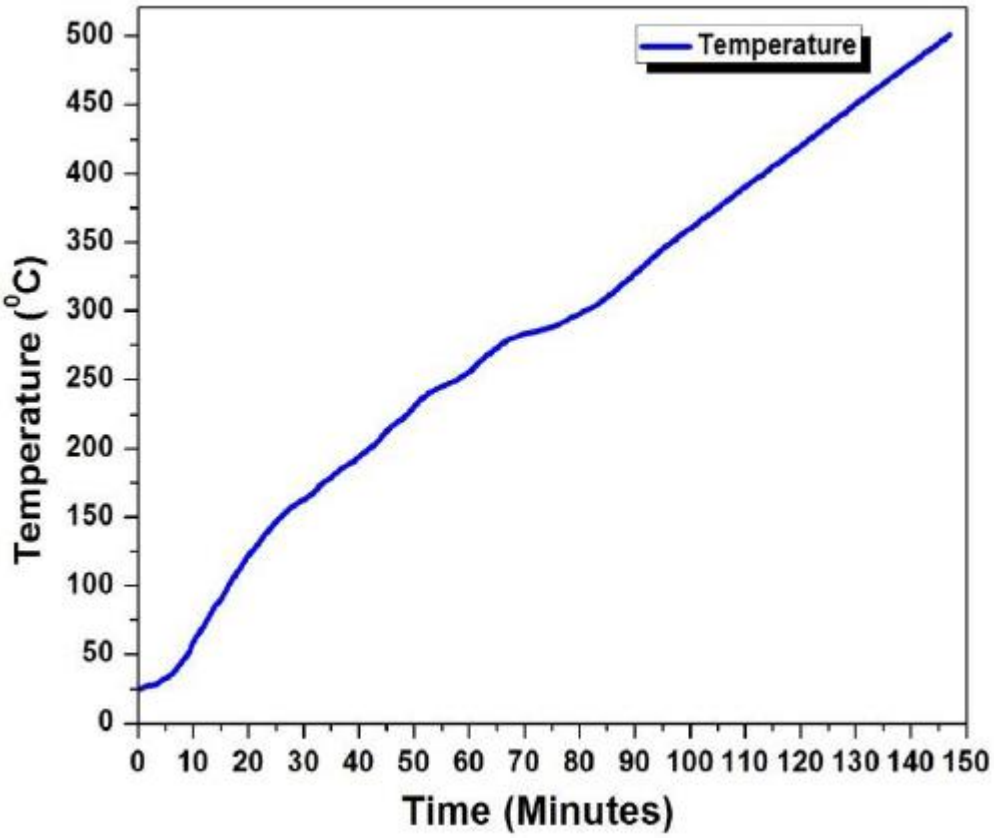


Fig. 4.2: Heating curve for the reactor

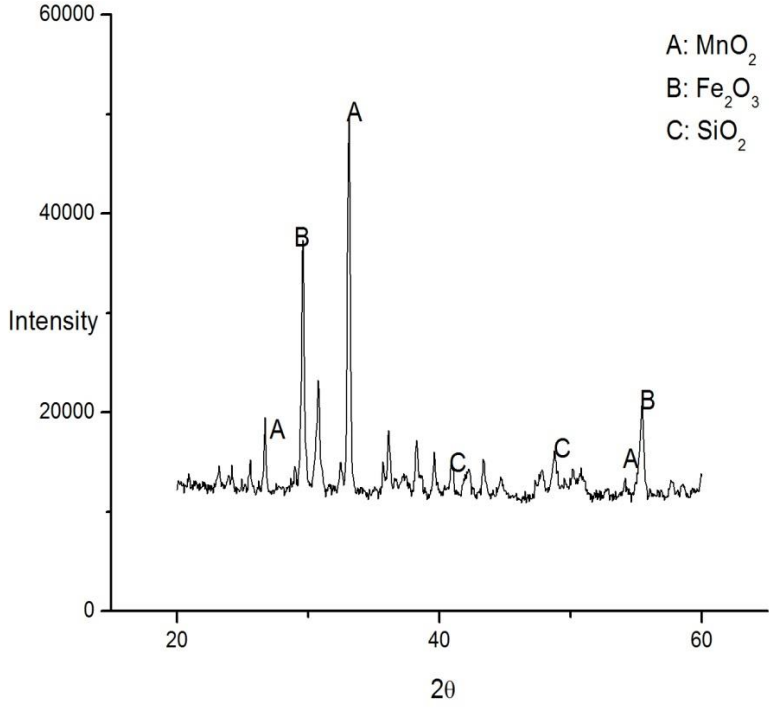


Fig. 4.3: XRD Plot of the Original Sample

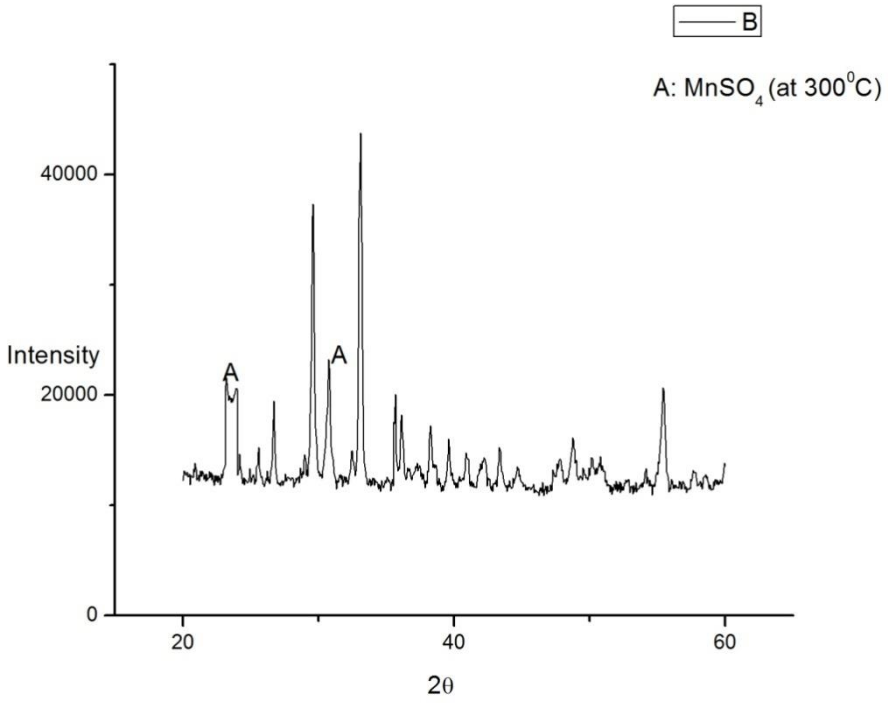
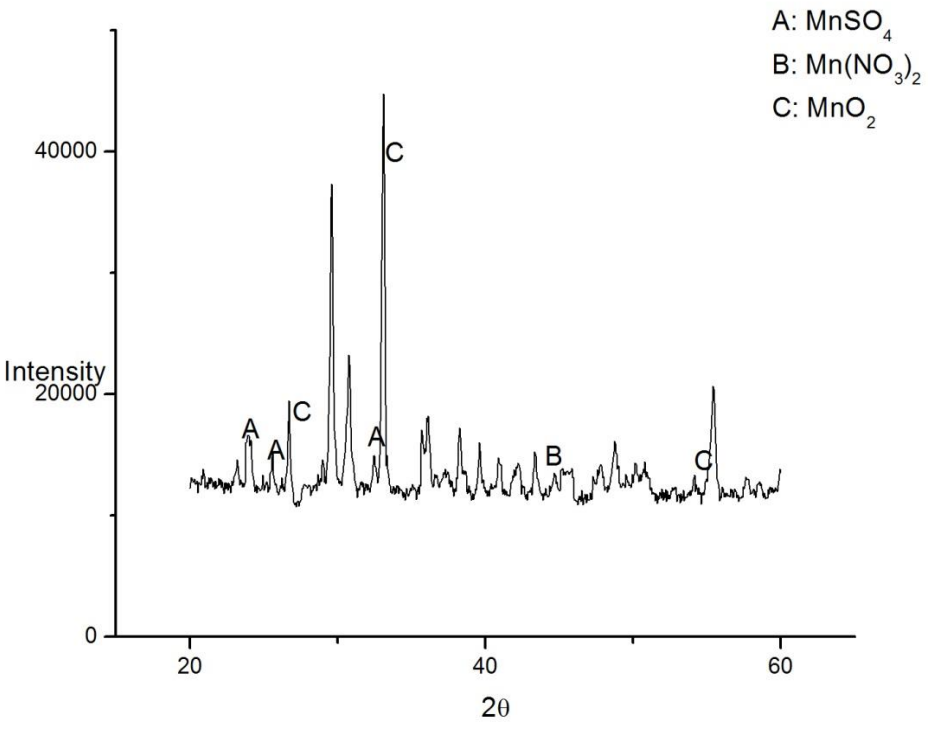
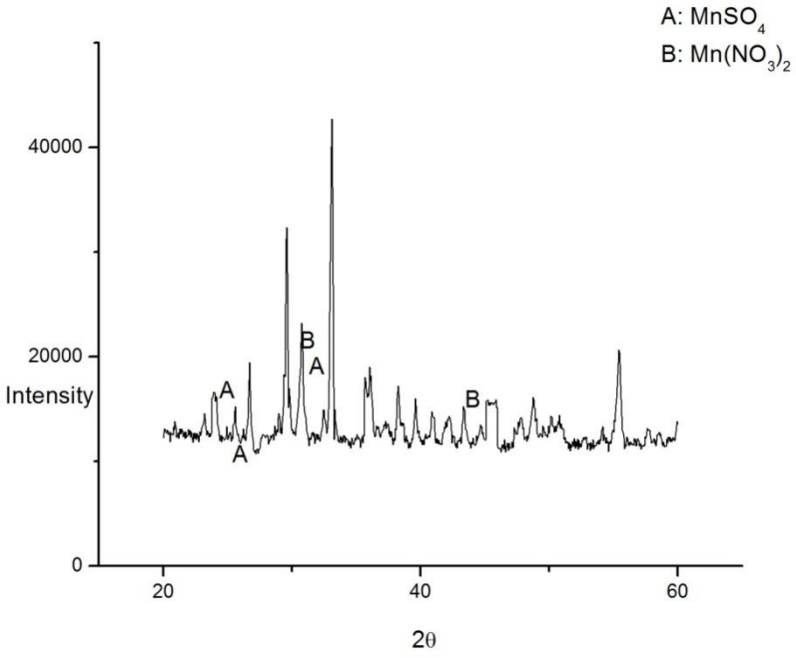


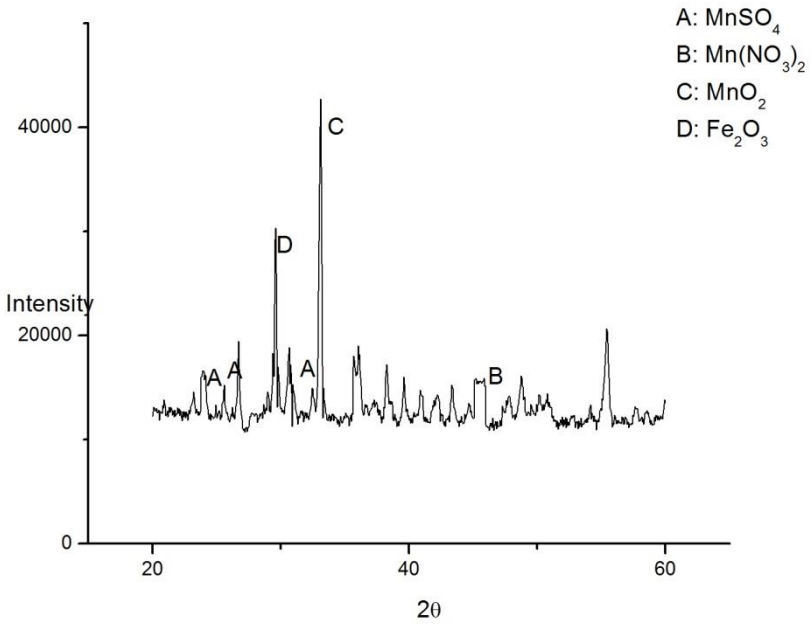
Fig. 4.4: XRD Plot for the Sample after Reaction at 300^0C.



(a) 200^0C, 15minutes

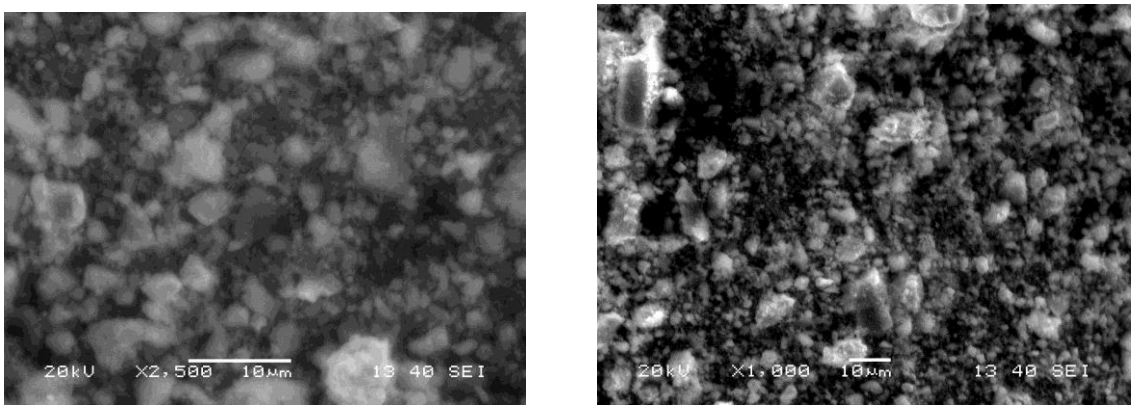


(b) 200^0C, 30 minutes



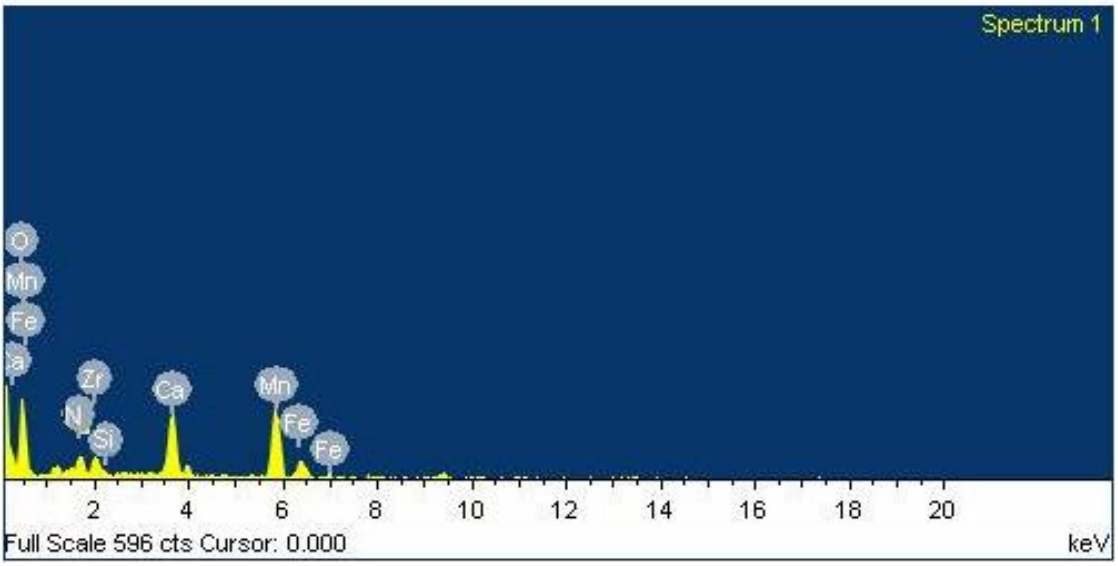
(c) 200^0C, 45 minutes

Fig.4.5: XRD Plots for Simultaneous Abatement of SO_2 and NO_2 at Different Residence Time

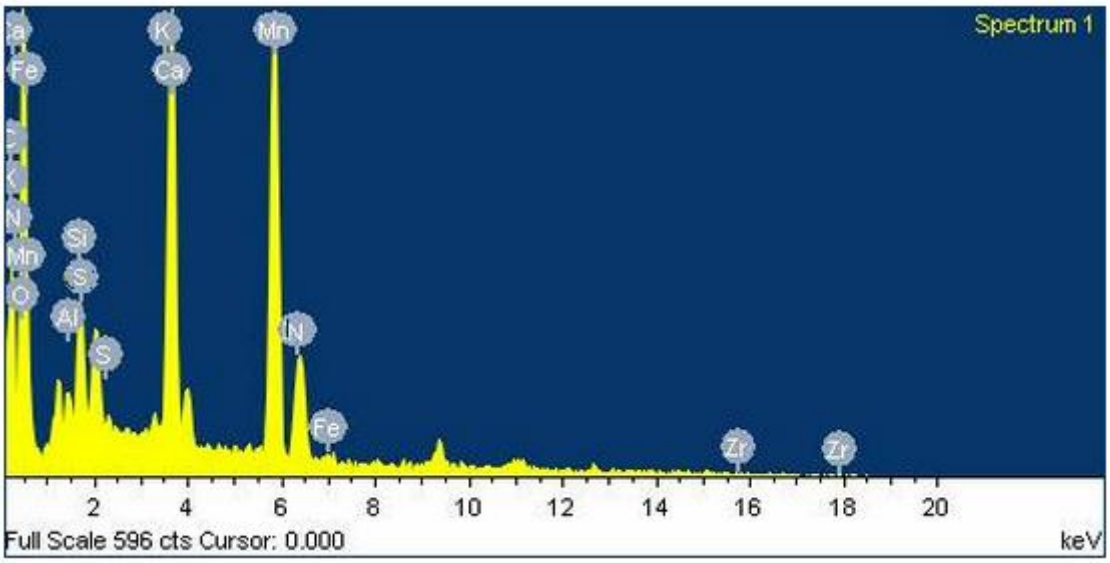


(a) Before Reaction (b) After Reaction.

Fig4.6: FESEM images observed before and after reaction.



(a) Original sample



(b) After 30 minutes (200^0C)

Fig.4.7 EDX analysis of samples as observed before and after reactions.

Chapter-5

Conclusion and Future Scope

Two sets of experiments were carried out in this project. The first, where only sulphur dioxide was fed with air as the primary fluidizing media at a temperature of 300^0C.And the other where both SO_2 and NO_2 are fed together at 200^0C. The residence time was varied between 15 to 45 minutes. From the results it can be concluded that more amount of sulphur dioxide is abated at higher temperature like 300^0C. This can be attributed to the fact that at higher temperature, the complex bonds between manganese oxides tends to break and form simple manganese oxide. This manganese oxide can easily react with the sulphur dioxide present. Also, on increasing the residence time, the sulphur abatement was increased due to the increased solid-gas contacting time.

Thus the experiment proved to be successful as it was able to show successful abatement of sulphur dioxide using natural manganese ore in a fluidized bed reactor. However, a more detailed study was not possible because of a lot of physical difficulties faced during the experiments. The continuous problems of leakage through the pipes and non-functioning of the rotameter delayed the experiments. The damage of the coil heater prohibited us from heating the air media thus restricting our study to only reactions with cold air.

The accuracy of the experiment could be more properly analyzed if the percentage composition of sulphur dioxide in the fed gas could be calculated before and after the experiments. This was however not carried out because of lack of a gas analyzer.

5.1 Future Scope

- To study the reactor with flue gas emitted from a plant.
- To study the various reaction kinetics involved in the fluidized bed to understand the working better.
- Making the FBR more efficient by studying the various parameters such as residence time, bed PSD etc.
- To study the abatement by measuring the concentration of SO_2 present in the gas.

Abbreviations

FBR**:** Fluidized Bed Reactor

NMO: Natural Manganese Ore

XRD: X-Ray Diffraction

FESEM: Field Emission Scanning Electron Microscope

EDX: Energy Dispersive X-Ray

References

[1] Public Health Statement Sulphur Dioxide,ATSDR,CAS#: 7446-09-5, December 1998.

[2] Szép, A. andHarja, M. Absorbtion of Sulphur Dioxide in Waste Calcium Carbonate Slurry.II. The Influence of the Parameters on the Absorption Rate,COFrROCA, (2006).

[3] Lee, K.T.; Mohamed, A.R.; Bhatia, S. and Chu, K. H. Removal of sulfur dioxide by fly ash/CaO/CaSO4 sorbents, Elsevier, Chemical Engineering Journal 114 171–177(2005).

[4] Galyan, D. Using limestone for cleaner air, Indiana University *Research & Creative Activity* 3 1998

[5] Lee, K. T.; Bhatia, S. and Mohamed, A. R. Removal of sulfur dioxide using absorbent synthesized from coal fly ash:Role of oxygen and nitrogen oxide in the desulfurization reaction, Elsevier, Chemical Engineering Science 60 3419 – 3423(2005).

[6] Rau, J; Tseng,H;Chiang, B; Wey, M. and Lin, Min-Der. Evaluation of SO2 oxidation and fly ash filtration by an activated carbon fluidized-bed reactor: The effects of acid modification, copper addition and operating condition, Elsevier, Fuel 89 732–742(2010).

[7] Ucan, H.; OZkan, G.;Bicer, A.and Pamuk, V. Removal of Sulphur dioxide in a periodically operating tickle bed reactor with activated carbon, IChem, Process Safety and Environmental Protection 83(B1): 47–49 (2005) .

[8] Gaur, V;Asthana, R and Verma, N. Removal of SO_2 by activated carbon fibers in thepresence of O_2 and H_2O, Elsevier, Carbon 44 46–60(2006).

[9] Lv, Y; Yu, X Shan-Tung, T; Yan, J and Dahlquist, E. Experimental studies on simultaneous removal of CO2 and SO2 in a polypropylene hollow fiber membrane contactor, Elsevier, Applied Energy, 97 283-288 (2012).

[10] Park,H; Deshwal, B.R.; Kim, I.W. and Lee, H.K.. Absorption of SO_2 from flue gas using PVDF hollow fiber membranes in a gas–liquid contactor, Elsevier, Journal of Membrane Science, 319 (2008)

[11] Jeong, K.S.; Park, T.S. and Hong S.C. "Simultaneous Removal of SO_x/NO_x in a fluidized bed reactor using Natural Manganese Ore" Journal of Chemical Technology and Biotechnology 76, 1080, 2001.

[12] Chkravarty, S; Dureja, V; Bhattacharya, G; Maity, S and Bhattacharjee , S "Removal of arsenic from gunpowder using low cost Manganese ore" Elsevier, 36 2002

[13] Arjmand, M.; Leion, H.; Mattison T. and Lyngfelt A. "Use of Manganese Ore in Chemical-Looping Combustion(CLC)-Effect on Steam Gasification" Elsevier, 8 56 2012.

[14] Mohapatra, D.; Mishra, D.; Mishra, S.P and Rao Choudhury, G. "Use of Oxide Minerals to abate fluoride from water" Elsevier, 275 355 2004.